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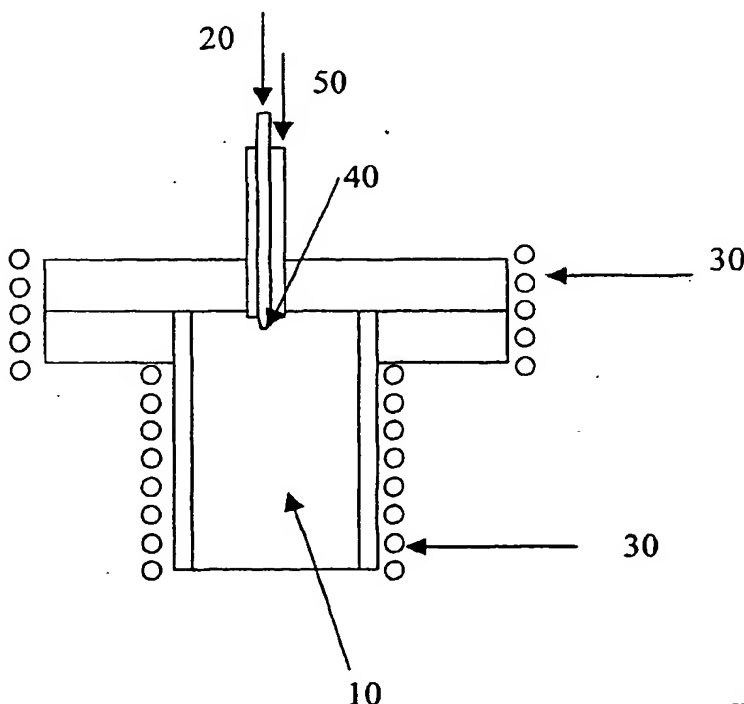
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(54) Title: FABRICATION OF HIGH CURRENT COATED HIGH TEMPERATURE SUPERCONDUCTING TAPES

(57) Abstract: The fabrication of high current coated high temperature superconducting tapes utilizing vaporized rare earth, barium and copper tetramethyl heptanedionates is disclosed.



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## Fabrication of High Current Coated High Temperature Superconducting Tapes

### Background Of The Invention

#### 1. Field of the Invention

This invention relates generally to an apparatus and method for the production of high temperature superconducting materials. More specifically, the invention relates to the preparation of high current and high current density HTS materials prepared by MOCVD deposition of dissimilar precursor materials.

#### 2. Description of the Related Art

High temperature superconducting (HTS) materials have immense potential for use in electric power, electronics, and medical industries. Presently, the HTS material that is manufactured in considerable quantities by industry is based on (Bi,Pb)SrCaCuO (BSCCO) superconductor. This material and the process used to manufacture it have proven to be expensive. Furthermore, the properties of this material degrade quickly in the presence of magnetic fields that are generated in a number of electric power devices.

ReBaCuO (Re = rare earth) superconductor is being developed as a potential alternative to the BSCCO superconductor. When fabricated in the form of a thin film coated on a metal substrate (HTS coated conductor), this material exhibits superior current carrying capability compared to BSCCO.

Several deposition processes are being developed to fabricate HTS Coated conductor. In general, thin film deposition techniques can be classified into two major categories: (1) physical vapor deposition (PVD) and (2) chemical processes (see "The Materials Science of Thin Films", Milton Ohring, Academic Press, 1992; S. L. Swartz, IEEE Transactions on Electrical Insulation, 25(5), 1990, 935; S. B. Krupanidhi, J. Vac. Sci. Technol. A, 10(4), 1992, 1569).

Most of the approaches are based on physical vapor deposition techniques where a source of HTS material is vaporized by means of (1) ablation with a high power laser, (2) evaporation using an electron-beam source, or (3) sputtering using high energy argon ions.

However, these techniques are limited in several ways. First, they are all limited by line of sight i.e. the vapors can coat the substrate only where they can 'see' the substrate, which means that the coated area is small. This limits the throughput of coated tape. Second, the composition of the coated film is limited to the composition of the material being vaporized. Third, the source material has to be maintained under vacuum causing refill to be difficult and in turns poses a problem for long-length manufacturing. Fourth, the source material has to be formed into a monolith, which adds cost to the process. Fifth, a high vacuum is needed which increases cost of capital equipment.

The chemical processes can further be divided into two subgroups i.e., chemical vapor deposition and wet chemical processes including sol-gel and metalorganic decomposition (MOD).

The sol-gel and MOD processes for deposition of thin films are popular because of their simplicity. Additionally, they provide molecular homogeneity, high throughput, excellent compositional control and low capital cost since no vacuum is required.

The limitations of wet chemical processes are thickness control, multiple steps for film formation (deposition, bakeout, & heat treatment as a minimum), need for repeat these multiple steps multiple times to build thick films, carbon residue incorporation in the films, difficulties in epitaxial growth in thick films, and evolution of harmful byproducts such as HF if fluorinated precursors are used.

A wide variety of source materials have been employed to form thin films, layers and coatings on substrates. These source materials include reagents and precursor materials of widely varying types, and in various physical states. Vapor deposition has been used widely as a technique to achieve highly uniform thickness layers of a conformal character on the substrate. In vapor phase deposition, the source material may be of initially solid form that is sublimed or melted and vaporized to provide a desirable vapor phase source reagent. Alternatively, the reagent may be of normally liquid state, which is vaporized, or the reagent may be in the vapor phase in the first instance.

These reagents may be used in mixture with one another in a multicomponent fluid, which is utilized to deposit a corresponding multicomponent or heterogeneous film material. Such advanced thin film materials are increasingly important in the manufacture of high-power electrical devices, microelectronic devices and in the emerging field of

nanotechnology. For use in such manufacturing processes, it is essential that the film morphology, composition, and stoichiometry be closely controllable. This in turn requires highly reliable and efficient means and methods for delivery of source reagents to the locus of film formation.

Examples of advanced thin film materials include high temperature superconducting (HTSC) materials including  $\text{YBa}_2\text{Cu}_3\text{O}_x$ ; wherein  $x$  is from about 6 to 7.3; bismuth-strontium-calcium-copper oxide and thallium-barium-calcium-copper oxide superconductors of varying stoichiometry ( $\text{BiSrCaCuO}$  and  $\text{TlBaCaCuO}$ ). Barium titanate,  $\text{BaTiO}_3$ , and barium strontium titanate,  $\text{Ba}_x\text{Sr}_{1-x}\text{TiO}_3$ , have been identified as ferroelectric and photonic materials with unique and potentially very useful properties in thin film applications of such materials.  $\text{Ba}_x\text{Sr}_{1-x}\text{Nb}_2\text{O}_6$  is a photonic material whose index of refraction changes as a function of electric field and also as a function of the intensity of light upon it. Lead zirconate titanate,  $\text{PbZr}_{1-x}\text{Ti}_x\text{O}_3$ , is a ferroelectric material whose properties are very interesting. The Group II metal fluorides,  $\text{BaF}_2$ ,  $\text{CaF}_2$ , and  $\text{SrF}_2$ , are useful for scintillation detecting and coating of optical fibers. Refractory oxides such as  $\text{Ta}_2\text{O}_5$  are coming into expanded use in the microelectronics industry;  $\text{Ta}_2\text{O}_5$  is envisioned as a thin-film capacitor material whose use may enable higher density memory devices to be fabricated.

Chemical vapor deposition is a particularly attractive method for forming thin film materials because it is readily scaled up to production runs and because the electronic industry has a wide experience and an established equipment base in the use of CVD technology, which can be applied to new CVD processes. In general, the control of key variables such as stoichiometry and film thickness, and the coating of a wide variety of substrate geometries is possible with CVD. Forming the thin films by CVD permits the integration of these materials into existing device production technologies CVD also permits the formation of layers of materials that are epitaxially related to substrates having close crystal structures.

CVD requires that the element source reagents, i.e., the precursor compounds and complexes containing the elements or components of interest be sufficiently volatile to permit gas phase transport into the chemical vapor deposition reactor. The elemental component source reagent must decompose in the CVD reactor to deposit only the desired element at the desired growth temperatures. Premature gas phase reactions leading to particulate formation must not occur, nor should the source reagent decompose in the lines

before reaching the reactor deposition chamber. When compounds are desired to be deposited, obtaining optimal properties requires close control of stoichiometry that can be achieved if the reagent can be delivered into the reactor in a controllable fashion. In this respect the reagents must not be so chemically stable that they are non-reactive in the deposition chamber.

Desirable CVD reagents therefore are fairly reactive and volatile. Unfortunately, for many of the materials described above, volatile reagents do not exist. Many potentially highly useful refractory materials have in common that one or more of their components are elements, i.e., the Group II metals barium, calcium, or strontium, or the early transition metals zirconium or hafnium, for which no or few volatile compounds well suited for CVD are known. In many cases, the source reagents are solids whose sublimation temperature may be very close to the decomposition temperature, in which case the reagent may begin to decompose in the lines before reaching the reactor, and it therefore is very difficult to control the stoichiometry of the deposited films from such decomposition-susceptible reagents.

When the film being deposited by CVD is a multicomponent substance rather than a pure element, such as barium titanate, lead zirconate titanate (PZT), lead lanthanum titanate (PLT), or the oxide superconductors, controlling the stoichiometry of the film is critical to obtaining the desired film properties. In the deposition of such materials, which may form films with a wide range of stoichiometries, the controlled delivery of known proportions of the source reagents into the CVD reactor chamber is essential.

In other cases, the CVD reagents are liquids, but their delivery into the CVD reactor in the vapor phase has proven difficult because of problems of premature decomposition or stoichiometry control. Examples include the deposition of tantalum oxide from the liquid source tantalum ethoxide and the deposition of titanium nitride from bis(dialkylamide)titanium reagents.

In the liquid delivery approach, the liquid or solid precursor is typically dissolved in a solvent, and the solution is stored, e.g., at ambient temperature and pressure. When the deposition process is to be run, the solution is transported to a high temperature vaporization zone within the CVD system, where the precursor is flash vaporized (along with the solvent), and the gas-phase precursor then is transported to the deposition zone, such as

a chemical vapor deposition reactor, containing a substrate on which deposition of the desired component(s) from the vapor-phase precursor composition takes place.

The liquid delivery technique has been found to be useful for deposition of multicomponent oxide thin films such as  $(\text{Ba}, \text{Sr})\text{TiO}_3$ ,  $\text{SrBi}_2\text{Ta}_2\text{O}_9$  (SBT),  $(\text{Pb}, \text{La})\text{TiO}_3$  (PLT) and  $\text{Pb}(\text{Zr}, \text{Ti})\text{O}_3$  (PZT) for example. In CVD processes developed for these and other compounds, it is desirable to dissolve all the precursors in a single solution, and vaporize them simultaneously, following which the vaporized precursor composition containing the respective components is transported to the deposition chamber, as described above.

Liquid delivery systems of varying types are known in the art, and for example are disclosed in U.S. Pat. No. 5,204,314 issued Apr. 20, 1993 to Peter S. Kirlin et al. and U.S. Pat. 5,536,323 issued Jul. 16, 1996 to Peter S. Kirlin et al., which describe heated foraminous vaporization structures such as microporous disk elements. In use, liquid source reagent compositions are flowed onto the foraminous vaporization structure for flash vaporization. Vapor thereby is produced for transport to the deposition reactor. The liquid delivery systems of these patents provide high efficiency generation of vapor from which films may be grown on substrates. Liquid delivery systems of such type are usefully employed for generation of multicomponent vapors from corresponding liquid reagent solutions containing one or more precursors as solutes, or alternatively from liquid reagent suspensions containing one or more precursors as suspended species.

The simplicity of such liquid delivery approach has been fortuitous, because each component in this system of metalorganic precursors can be treated identically in the respective solution-forming, vaporization and transport steps of the process. Thus, in such a compatible system of multiple, well-behaved precursors, (i) the precursors can be dissolved in the same solvent with high solubility, (ii) the precursors maintain their identity in the single solution, without deleterious chemical reactions with the solvent or net ligand exchange with each other, (iii) the precursors can be efficiently vaporized under the same temperature flow, pressure and ambient (carrier) gas conditions, and (iv) the CVD deposition process can be performed using a fixed ratio of the CVD precursors in the solution, distinct advantage since the relative proportions of the respective components cannot be easily quickly changed.

CVD using metalorganic precursors (MOCVD) is used for fabrication of films of various materials including HTS. However, MOCVD has yet to be shown to be a viable approach to achieve high current and high current density with HTS Coated conductors because suitable MOCVD apparatus and process has not been developed.

Therefore, an object of this invention is to provide an MOCVD Process and MOCVD System to produce HTS Coated Conductors suitable for use in high current and high current density environments.

Other objects and advantages of the invention will be more fully apparent from the ensuing disclosure and appended claims.

#### Summary of the Invention

The present invention relates to the use of a metal organic chemical vapor deposition (MOCVD) process for fabrication of coated HTS conductors. In a MOCVD process, chemical precursors of the constituent elements are vaporized at a low temperature and the vapors are deposited on a heated substrate to form the HTS film. The equipment can be designed for the vapors to flow over a large area i.e. a long-length of tape can be coated instantaneously or a number of tapes can be coated in parallel, both of which result in high throughput. The precursors of individual elements of the HTS material can be mixed in an infinite number of combinations. Therefore, the composition of the HTS film can be tailored to that preferred to achieve specific performance parameters. The precursors are maintained outside the deposition chamber under ambient conditions. Therefore, refill of precursors is very simple which is important for long length manufacturing. The precursors need not be formed into any shape, which does not add extra cost. MOCVD is performed at a pressure much higher than that used for PVD techniques and so, cost of capital equipment is relatively low.

#### Brief Description of the Drawings

Figure 1 is a schematic drawing of the vaporizer showing the orifice and heating elements.

Figure 2 is a schematic drawing of the deposition reactor showing the showerhead, the oxygen injector and the heating and cooling coils.



Figure 3 is a chart showing the current-voltage curve from a high-current YBC on metal substrate prepared utilizing the inventive process.

Figure 4 is a chart showing the performance of present generation HTS materials and of YBC and of on a metal substrate prepared utilizing the inventive process, in magnetic fields of interest for electric-power applications.

#### Detailed Description of the Invention

The selection of the precursors is the most critical step for successful deposition of complex oxide films. The ideal precursors for MOCVD have to meet the requirements of high vapor pressure at low vaporization temperatures, low decomposition temperatures, large "window" between vaporization and decomposition temperatures, no contamination from organic constituents of the precursors, stability under ambient conditions and nontoxicity. In the present invention, tetramethyl heptanedionates have been used as precursors to grow the complex layered structure films.

A liquid precursor is preferred to achieve high performance in HTS coated conductors fabricated by MOCVD. Advantages of liquid precursors over solid precursors include a single point of temperature control for vaporization, longer period of stability and easy refill, both of which are critical for long-length tape manufacturing, and higher precursor feed rates, which is important for high rates of deposition. Precursors that are especially useful in the innovative process are tetramethyl heptanedionate compounds of yttrium (or other rare earth such as Sm, Nd, Yb, Eu, Gd, Dy, Ho, Er), barium and copper. The Ba compound is preferably adducted with a compound such as phenanthroline to assure long-term stability. Each compound is individually dissolved in solvents such as tetrahydrofuran and isopropanol. Both THF and isopropanol are required to dissolve the Y and Ba compounds whereas THF alone is sufficient to dissolve the Cu compound. When the precursors have dissolved, the individual solutions are mixed together.

Tetramethyl heptanedionates of yttrium, barium [adducted with phenanthroline] and copper are obtained from InOrgatech, Mildenhall, Suffolk, U.K. The Y compound is dissolved in solvent containing 2 parts of THF and 1 part isopropanol. The Ba compound is dissolved in a solvent containing 3.5 parts THF and 1 part isopropanol. The Cu compound is dissolved only in THF.

When the individual precursors are dissolved they are mixed together in a ratio determined by the desired composition of the thin film. It is one of the particular benefits of the process that the film characteristics can be varied over a wide range by modifying the ratio of the precursors in the combination. The molarity of overall solution is in the range of from about 0.003 M/l to about 0.03 M/l.

The ratio of the rare earth, Ba and Cu compounds, as determined by the elemental ratio in the precursor solution should be between 1 to 1.65 – 2.65 to 3, preferably 1 to 2 – 2.3 to 3, and most preferably 1 to 2.15 to 3. The three solutions are combined by low shear mixing to form a uniform solution.

The liquid precursor solution is then pumped at a constant rate of from about 0.1 to about 10 ml/min into the vaporizer using a low-flow rate, high-pressure pump such as a HPLC (High Pressure Liquid Chromatography) pump. The pump should be capable of delivery low flow rates with a high accuracy and without pulsation. The wetted components of the pump should not react with the precursor solution. The rate of introduction will of course depend on the size of the vaporizer and deposition reactor. We have found that a rate of approximately 0.25 ml/min is suitable for deposition rate of about 2 microns/hour.

An important component of the MOCVD system is the vaporizer. The vaporizer used to flash evaporate a liquid precursor has to be maintained at a steady temperature. More importantly, the vaporizer should be maintained clog-free. Several designs of vaporizer including commercially available vaporizers such as MKS Model # DLI25BS99 have failed for use with the liquid precursors of the invention because of vaporizer clogging by the Ba precursor. It is also important that the vaporizer be designed to avoid streaming of the precursor solution, which is caused by suction of the solution by the vacuum in the system. Further, the vaporizer and has to be designed to avoid deposits of the precursor.

Referring to Figure 1, the vaporizer 10 is a cylindrical vessel constructed of non-reactive materials. Mounted at one end of the cylinder is an inlet means for the introduction of precursor solution to the vaporizer. The precursor is preferably delivered to the vaporizer through small bore tubing 20. The tubing is maintained wet using solvent when the vaporizer is not in operation to avoid clogging. Heating means 30 are placed around the exterior of the vaporizer body to maintain a high and even temperature distribution.

The precursor entry tubing ends in an orifice tip 40 with a diameter in the range of from about 10% to about 50% of the diameter of the delivery tubing. This narrow opening builds pressure and prevents suction of the precursor by the vacuum in the vaporizer. A typical orifice opening is from about 0.001 to about 0.005 inch inside diameter.

The delivery tubing is surrounded by an annular carrier gas delivery means 50, typically in the form of annular tubing surrounding the precursor delivery means 20. The carrier gas, typically argon, enters the vaporizer through delivery means 50 and is used to push the precursor exiting from nozzle 40 downward away from the orifice and into the body of the vaporizer 10.

The region of the vaporizer above the orifice is minimized to prevent precursor deposits.

The solution of mixed precursors is rapidly heated in the vaporizer to a temperature in the range of from about 180 to about 300° C, preferably from about 210 to about 270° C, and most preferably from about 230 to about 240° C and is pumped to a vaporizer. It enters the vaporizer through tubing swaged to a nozzle of about 0.004" ID orifice where the solution is flash vaporized. The pressure in the feed tubing is in the range of from about 0 to about 15 psi, preferably from about 0 to about 10, and most preferably from about 0 to about 5 psi. The pressure in the vaporizer is in the range of from about 1 to about 15 Torr, preferably from about 1 to about 10 Torr, and most preferably from about 2 to about 5 Torr.

A tubing of very small diameter, shaped into a small orifice at the tip to build enough pressure to avoid sucking of precursor by reactor vacuum is preferred (too small a diameter will end up in clogging, too large a diameter will prevent pressure buildup). The tip of the tubing has to be placed in a high temperature zone in the vaporizer. If it is at a low temperature, the precursors will not vaporize instantaneously. The region above the tip of the delivery tubing should be minimized and should be maintained at a high temperature, both for avoiding formation of precursor deposits. The outlet for the argon 'push gas' should be placed around the orifice to push the vaporized precursors downward. The tubing should be cleaned with solvent such as THF at high pressure after the deposition run to avoid clogging. The tubing should be maintained wet prior to ramping the vaporizer to set temperature. The tip of the tubing should be maintained approximately at 230° to 240° C.

The cross-section of the delivery tube should not be decreased beyond the vaporizer so as to avoid deposits of the precursor.

In a preferred embodiment, the orifice is sized to inject approximately 0.25ml/min of precursor into the vaporizer. In another preferred embodiment an annular inert gas injector is used to force the precursor vapors downward away from the orifice. In general, it is useful to supply the inert gas to the vaporizer at a rate of about 500 to 4000 ml/min. Argon is the preferred inert gas but nitrogen or other inert gas may be used.

The vaporizer is connected to the deposition reactor through small-bore tubing. The minimum diameter of the tubing is 0.25"; the maximum is 5". Preferably, the diameter of the tubing is in the range of from about 1 to about 1.5".

Referring to Figure 2, vaporized precursors are received from vaporizer 10 [not shown] through delivery tubing 60 along with introduced oxygen. The vaporized precursors and oxygen are dispersed into the deposition reactor [not shown] by means of showerhead 70. The vaporized precursors are maintained at an appropriate temperature prior to entry into the showerhead 70 by heating means 80 placed around the delivery tubing. The temperature of the vaporized precursors is maintained at an appropriate temperature as it passes through the showerhead 70 by heating means 90 and cooling means 80.

A high temperature valve with a direct line of sight and uniform bore is used between vaporizer and reactor. The path of the precursor vapor should not be obstructed prior to injection into the reactor showerhead. Oxygen must be introduced close to the precursor injection point and is preferably uniformly directed over the entire showerhead. A showerhead in the form of a disc with small perforated holes is a suitable way to achieve such an uniform flow. If it is introduced non-uniformly, the film growth will be non-uniform when depositing on large areas. The entire delivery line from the vaporizer to showerhead should be maintained between 230° and 270° C.

The precursor vapors are uniformly injected over the entire substrate area using a showerhead. The showerhead is preferably constructed with numerous fine openings; the total cross sectional area of the openings should be less than the cross sectional area of the precursor delivery tubing. The perforations should have a certain length to them so as to direct the flow downward. The showerhead should be maintained in a temperature range of 230° to 270° C prior to film deposition. A shutter should be used between the showerhead

and the substrate heater prior to film deposition so as to prevent any film formation at a lower temperature while the substrate heater is ramped up to deposition temperature. The showerhead may not reach the preferred temperature range mentioned above with the shutter in place. A suitable way to achieve the desired showerhead temperature is to install a heater around the showerhead itself. However, after the shutter is opened the showerhead may overheat due to exposure to the heat from the substrate heater. To avoid this problem, it is desirable to install a cooling coil around the showerhead. To facilitate cooling, the showerhead should be constructed of a single block of metal, the cooling coil welded to it and the heating coil placed around the cooling coil.

The vaporized precursors are delivered from the vaporizer to the deposition chamber through a showerhead. The showerhead is preferably constructed with numerous fine openings, the total cross sectional area of which should be less than the cross sectional area of the precursor delivery tubing. The perforations have a certain length to them so as to direct the flow downward. The length should be sufficient to direct the flow onto the substrate but not so long as to prevent adequate spread. Lengths of from about 1 to about 10 mm have been found useful. A cooling coil welded to the showerhead and a heating coil surrounding the showerhead to maintain constant temperature ( $230^{\circ}\text{C}$  to  $270^{\circ}\text{C}$ ) at all times. Prior to film deposition, when the shutter is closed, the heating coil heats up the showerhead.

During deposition, when the shutter is open and the showerhead is exposed to the substrate heater, the cooling coil cools the showerhead.

To facilitate cooling, the showerhead should be constructed of a single block of metal and the cooling coil be welded to it and the heating coil placed around the cooling coil.

A high temperature valve with a direct line of sight and uniform bore should be used between vaporizer and reactor. The path of the precursor vapor should not be obstructed prior to injecting to the showerhead.

Oxygen must be introduced to the reactor along with the precursors, preferably uniformly directed over the entire showerhead. A ring with small perforated holes is a suitable way to achieve such an uniform flow. If introduced nonuniformly, the film growth will be nonuniform when depositing on large areas. The entire delivery line from the vaporizer to showerhead should be maintained between  $230^{\circ}\text{C}$  and  $270^{\circ}\text{C}$ .

The substrates to be coated are heated to about 700° to 850° C, preferably about 750° to 800° C. Lower reactor pressure in the lower portion of the acceptable range, oxygen partial pressure in the lower portion of the acceptable range and substrate temperature in the higher portion of the acceptable range are found to favor formation of high quality HTS films on commercial substrates.

The substrate may be any metallic substrate conventionally used as a substrate for HTS films. Stainless steel or nickel alloy are particularly well suited. The substrate heater should be placed at a distance of about 15 to 30 mm from the showerhead. If it is placed too close, the showerhead will overheat due to the heat from the heater. Also, the precursor may decompose and result in deposition of particles on the substrate. If it is kept too far, the thickness of the film will be reduced and the precursors may condense into their individual constituents.

The MOCVD reactor is preferably of cold-wall type i.e. the walls of the reactor are not heated. The pressures in the reactor and the by-pass line are maintained constant using throttle valves that are automatically controlled by pressure readings using capacitance manometers.

At reactor start-up, and until the reactor reaches optimum operating conditions, the vaporized mixture of precursors is shunted to a by-pass line maintained at the same pressure as that in the MOCVD reactor. After the substrates are heated to deposition temperature, the vapor flow is switched to the reactor input line. This procedure is accomplished using two high temperature valves.

A pressure of 1 to 5 Torr, preferably 1 to 2.5 Torr, most preferably 1.6 Torr is maintained in the reactor (as well as in the by-pass line). The low reactor pressure in the presence of high gas flow rates is preferably achieved using a roots blower-vacuum pump system.

Oxygen is flowed into the reactor to achieve a partial pressure of about 0.3 to 1 Torr, preferably 0.35 to 0.8 Torr, most preferably about 0.55 Torr.

After deposition, the films are cooled at a controlled rate in a high partial pressure of oxygen (100 to 760 Torr) to room temperature. In general, it will require from about 30 to about 60 minutes to complete the cooling.

Using the process and system design described above, critical currents of almost 100 A (130 A/cm width) and current density of 1.3 MA/cm<sup>2</sup> have been achieved for the first time in HTS coated conductor. Figure 3 demonstrates the high performance results achieved in a YBC coated conductor fabricated by the claimed process.

Figure 4 demonstrates that high performance can be achieved in HTS YBC coated conductor fabricated utilizing the inventive process, in high magnetic fields at 75 K and 64 K. The performance of the coated conductor far exceeds that of present generation BSCCO-based HTS tape technology and meets the requirements of various electric power devices.

Having described the invention, the following example is provided to illustrate a specific application of the invention including the best mode now known to perform the invention. This specific example is not intended to limit the scope of the invention described in this application.

#### Example

Tetramethyl heptanedionates of yttrium, barium [adducted with phenanthroline] and copper are obtained from Inorgatech, Mildenhall, Suffolk, U.K. The Y compound is dissolved in solvent containing 2 parts of THF and 1 part isopropanol. The Ba compound is dissolved in a solvent containing 3.5 parts THF and 1 part isopropanol. The Cu compound is dissolved only in THF. The molarity of overall solution is 0.03 M/l.

The liquid components are combined at room temperature in an ultrasound mixer in the ratio of 1 part Y composition, 2.15 parts Ba composition and 3 parts Cu composition. The mixed liquid precursor is pumped at a rate of 0.25 ml/min through a HPLC pump. From the pump, the precursor is pumped through 0.0625" OD, 0.010" ID stainless steel tubing at a pressure of 5 psi to the vaporizer.

The mixed component precursor enters the vaporizer through the nozzle that is made from a 0.0625" OD, 0.01" ID tubing swaged to an ID of 0.004" at tip. The tip is placed in a vaporizer that is maintained at 240<sup>0</sup> C using a band heater and heating jackets. The orifice is surrounded by an annular argon gas injector. The argon is supplied to the vaporizer at the rate of 1000 ml/min.

The vaporized precursors are transferred to the reactor through 1.5"- diameter stainless steel tubing. The composition is maintained at a temperature of 240<sup>0</sup> C while in the delivery tubing.

The reactor, a cold wall type, is maintained at a pressure of 1.6 Torr. The composition is introduced into the reactor through a showerhead. Heating and cooling coils to maintain the temperature in the range of about 235° C surround the showerhead. In this example the showerhead is comprised of two 2.75" con-flat flanges bolted together. The top flange is connected to the tubing from the vaporizer. The bottom flange has perforations disposed uniformly on the surface. The plate has a thickness of about 6 mm, and the perforations are about 0.02 to 0.03" in diameter. The length of the perforation is about 6 mm, sufficient to direct the flow downward. The showerhead can deliver precursors over a diameter of 2.5 cm over the substrate.

Oxygen is introduced into the showerhead at a flow rate of 500 ccm.

The substrate, comprising of an Inconel 625 metal tape, is introduced into the reactor and heated, utilizing a substrate heater, to a temperature of 775° C.

The vaporized precursor entering the reactor through the showerhead contacts the substrate and is deposited as a thin film.

The resulting coated substrate is cooled to ambient temperature in an oxygen rich atmosphere over a period of 1 hour.

Obviously, many modifications and variations of the present invention are possible in light of the above teachings. It is therefore to be understood that, within the scope of the appended claims, the invention may be practiced otherwise than as specifically described.



## Claims

1. A process for the production of HTS conductors consisting of a metallic substrate and a thin film coating of rare earth-barium-copper oxides and capable of conducting currents greater than 100 A/cm width and current densities of greater than 1 MA/cm<sup>2</sup> at 77 K, self field comprising

- a) separately dissolving a rare earth, barium and copper tetramethyl heptanedionates in a suitable solvent;
- b) combining the solutions from step a);
- c) vaporizing the mixed solution of step b) by flash vaporization in a first vessel;
- d) placing the substrate to be coated in the second vessel;
- e) heating the substrate;
- f) injecting the vaporized mixed solution through a showerhead into the second vessel where the vaporized coating components contact and are deposited on the substrate surface; and
- g) slowly cooling the coated substrate.

2. The process of claim 1 wherein the molarity of the precursor solution in step b) is approximately 0.03 M/l.

3. The process of claim 1 wherein the ratio of the rare earth compound is dissolved in a solvent containing 2 parts by weight tetrahydrofuran and 1 part by weight isopropanol; the barium compound is dissolved in a solvent containing about 3.5 parts by weight tetrahydrofuran and 1 part by weight isopropanol and the copper compound is dissolved in tetrahydrofuran.

4. The process of claim 1 wherein the ratio of the rare earth, Ba and Cu compounds is in the range of from about 1:1.65:3 to about 1:2.65:3.

5. The process of claim 1 wherein the ratio of the rare earth, Ba and Cu compounds is in the range of from about 1:2:3 to about 1:2.3:3.

6. The process of claim 1 wherein the ratio of the rare earth, Ba and Cu compounds is about 1:2.15:3.

7. The process of claim 1 wherein the temperature in the first vessel is in the range of from about 180° C to about 300° C.
8. The process of claim 1 wherein the temperature in the first vessel is in the range of from about 210° C to about 270° C.
9. The process of claim 1 wherein the temperature in the first vessel is in the range of from about 230° C to about 240° C.
10. The process of claim 1 wherein the temperature of the showerhead is maintained in the range of from about 210° C to about 270° C.
11. The process of claim 1 wherein the temperature of the showerhead is maintained in the range of from about 230° C to about 240° C.
12. The process of claim 1 wherein the pressure in the second vessel is maintained in the range of from about 1 to about 5 Torr.
13. The process of claim 1 wherein the pressure in the second vessel is maintained in the range of from about 1.5 to about 2.5 Torr.
14. The process of claim 1 wherein the pressure in the second vessel is maintained at about 2.0 Torr.
15. The process of claim 1 wherein the oxygen partial pressure in the second vessel is maintained in the range of from about 0.3 to about 1 Torr.
16. The process of claim 1 wherein the oxygen partial pressure in the second vessel is maintained in the range of from about 0.35 to about 0.8 Torr.
17. The process of claim 1 wherein the oxygen partial pressure in the second vessel is maintained at about 0.55 Torr.
18. The process of claim 1 wherein the distance between the showerhead and the substrate is in the range of from about 15 to about 30 mm.
19. The process of claim 1 wherein the rare earth is yttrium.
20. A process for the production of HTS conductors consisting of a metallic substrate and a thin film coating of yttrium-barium-copper oxides and capable of conducting currents greater than 100 A/cm width and current densities of greater than 1 MA/cm<sup>2</sup> at 77 K, self field comprising

- a] separately dissolving yttrium, barium and copper tetramethyl heptanedionates in suitable solvents;
- b] combining the solutions from step a];
- c] introducing the combined solutions to a vaporizer at a flow rate of about 0.25 ml/min;
- d] vaporizing the mixed solution of step b] by flash vaporization in a first vessel;
- e] placing the substrate to be coated in the second vessel;
- f] heating the substrate to a temperature in the range of from about 700° C to about 850° C;
- g) injecting the vaporized mixed solution through a showerhead into the second vessel where the vaporized coating components contact and are deposited on the substrate surface; and
- h] slowly cooling the coated substrate.

21. An HTS conductor capable of conducting currents greater than 100 A/cm width and current densities of greater than 1 MA/cm<sup>2</sup> at 77 K, self field comprising a metallic substrate and a thin film coating comprising rare earth-barium-copper oxides.

22. An HTS conductor produced by the process of claim 1 and capable of conducting currents greater than 100 A/cm width and current densities of greater than 1 MA/cm<sup>2</sup> at 77 K, self field comprising a metallic substrate and a thin film coating comprising rare earth-barium-copper oxides.

23. A vaporizer suitable for use in preparing HTS conductors by MOCVD processes comprising a cylindrical body, an inlet means for a liquid to be vaporized mounted on one end of the vaporizer, an annular gas inlet means mounted on one end of the vaporizer and surrounding the liquid inlet means, and an outlet means for transferring the vaporized liquid and gas to a deposition reactor.

24. A deposition reactor suitable for use in preparing HTS conductors by MOCVD processes comprising a cylindrical body, a delivery means for delivering vaporized deposition composition to an inlet means for a vaporized deposition composition, an inlet means for

oxygen rich gas, a heating means, a cooling means, a substrate holding means for holding a substrate to be coated by the vaporized deposition composition, a means for inserting and removing the substrate to be coated, and an outlet means for waste deposition composition wherein the inlet means for the vaporized deposition composition is a showerhead constructed with numerous fine openings, the total cross sectional area of which are less than the cross sectional area of the vaporized deposition composition delivery means, the perforations have a minimum length of about 1 mm, the cooling means is a cooling coil welded to the showerhead and the heating means is a heating coil surrounding the showerhead.

Figure 1

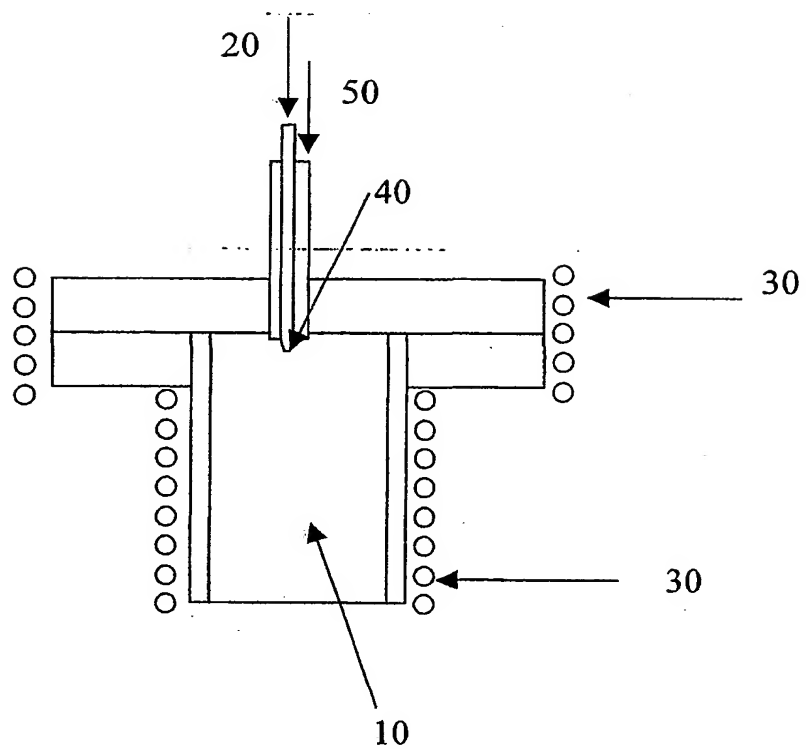


Figure 2

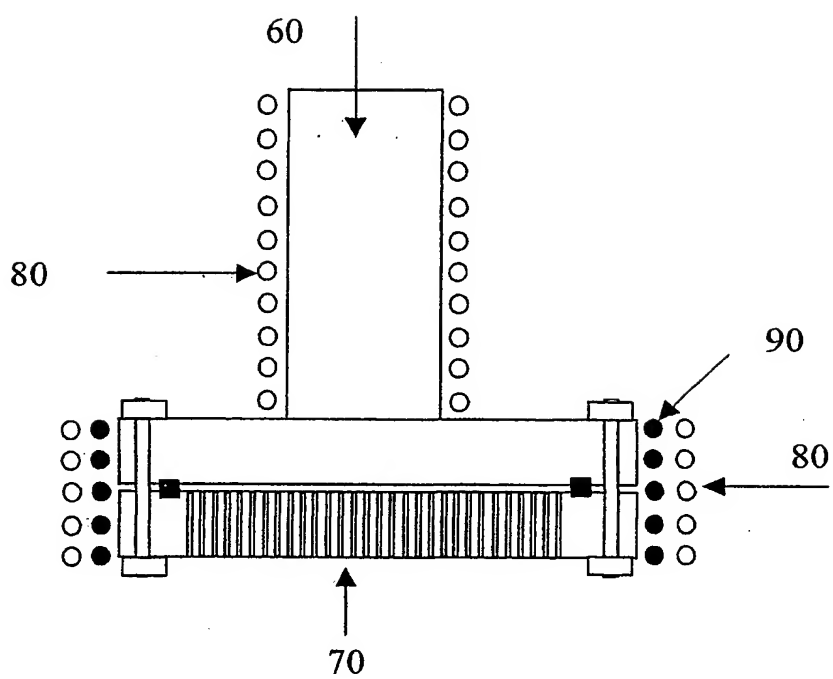


Figure 3

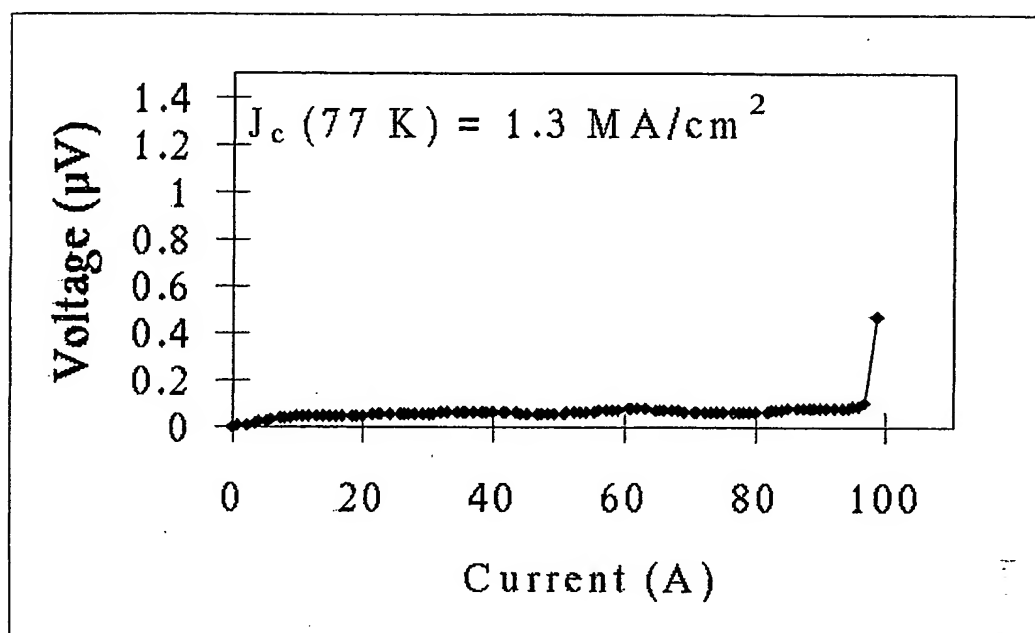
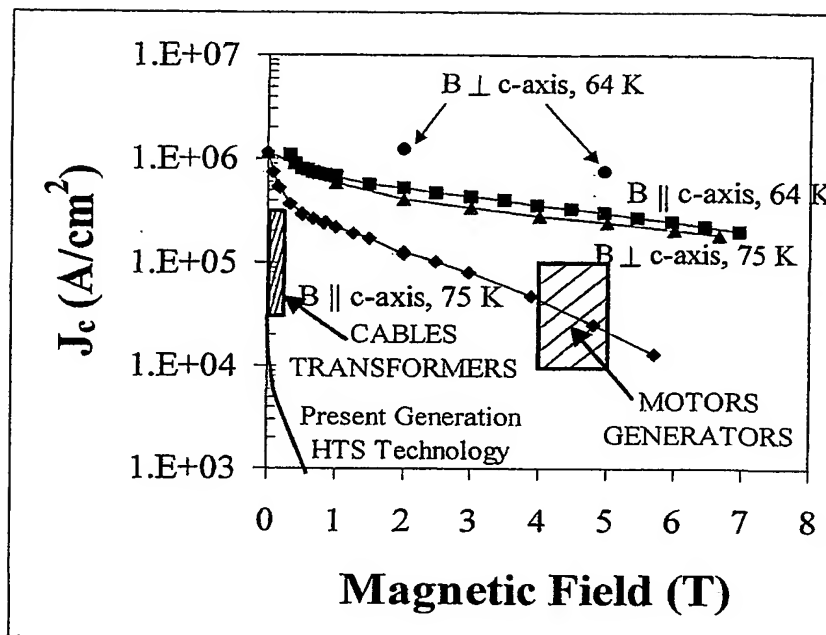


Figure 4





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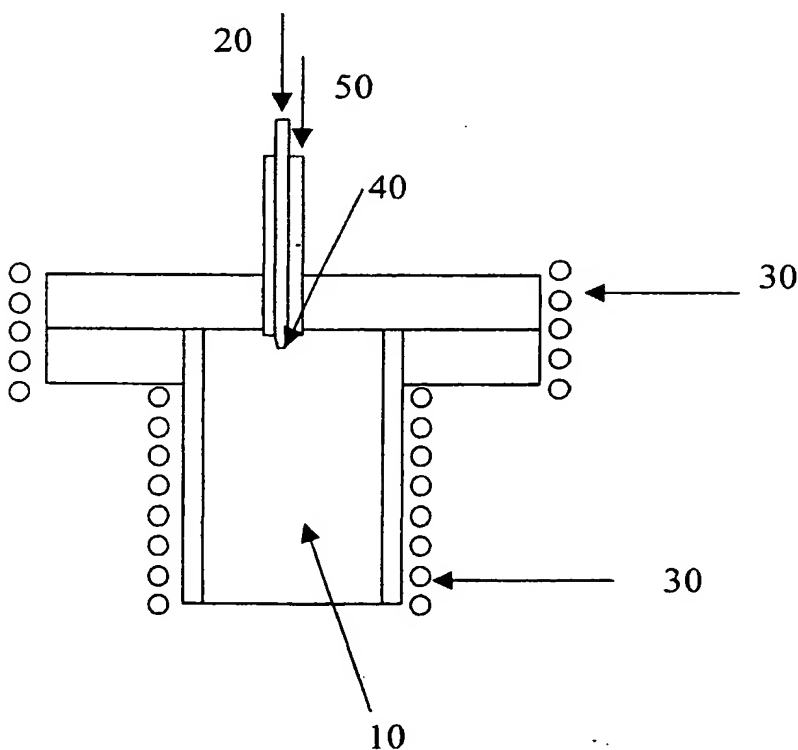
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[Continued on next page]

(54) Title: FABRICATION OF HIGH CURRENT COATED HIGH TEMPERATURE SUPERCONDUCTING TAPES



(57) Abstract: Precursor gases enter a vaporizer (10) including heating means (30) through tubing (20) and (50) which form nozzle (40) for forming an HTSC coating.

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## INTERNATIONAL SEARCH REPORT

International application No.

PCT/US01/41529

**A. CLASSIFICATION OF SUBJECT MATTER**IPC(7) : C23C 16/40; B05D 5/12  
US CL : 427/62,126.3,255.19,255.32

According to International Patent Classification (IPC) or to both national classification and IPC

**B. FIELDS SEARCHED**

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Documentation searched other than minimum documentation to the extent that such documents are included in the fields searched  
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N/A**C. DOCUMENTS CONSIDERED TO BE RELEVANT**

Category *	Citation of document, with indication, where appropriate, of the relevant passages	Relevant to claim No
Y	US 6,037,002 A (HINTERMAIER) 14 MARCH 2000, FIGURE 1 AND COL. 4, LINES 30-60	1-24
Y	US 5,653,806 A (VAN BUSKIRK) 05 AUGUST 1997, ABSTRACT, FIGURE 1 AND COL. 4, LINES 40-55	1-24
Y	US 5,376,594 A (COVINO-HRBACEK) 27 DECEMBER 1994, ABSTRACT AND COL. 2, LINES 10-40	1-24
Y	US 5,278,138 A (OTT ET AL.) 11 JANUARY 1994, ABSTRACT AND COL. 3, LINE 5 - COL. 6, LINE 55	1-24

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